

09/743244

Practitioner's Docket No. 55,542 (45107)

CHAPTER II

**TRANSMITTAL LETTER  
TO THE UNITED STATES ELECTED OFFICE (EO/US)**

**(ENTRY INTO U.S. NATIONAL PHASE UNDER CHAPTER II)**

<u>PCT/EP99/04841</u>	<u>9 July 1999</u>	<u>9 July 1998</u>
INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED

POROUS CERAMICS  
TITLE OF INVENTION

Klaus HECKMANN, Thomas ALBRECHT, and Thomas WENGER  
APPLICANT(S)

**Box PCT**  
**Assistant Commissioner for Patents**  
**Washington D.C. 20231**  
**ATTENTION: EO/US**

*NOTE: To avoid abandonment of the application, the applicant shall furnish to the USPTO, not later than 20 months from the*

**CERTIFICATION UNDER 37 C.F.R. 1.10\***

*(Express Mail label number is **mandatory**.)*

*(Express Mail certification is optional.)*

I hereby certify that this correspondence and the documents referred to as attached therein are being deposited with the United States Postal Service on this date January 5, 2001, in an envelope as "Express Mail Post Office to Addressee," Mailing Label Number TB338582618US, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

Peter F. Corless  
*(type or print name of person mailing paper)*

  
Signature of person mailing paper

**WARNING:** *Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.*

**\*WARNING:** *Each paper or fee filed by "Express Mail" **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. 1.10(b).  
"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.*

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priority date: (1) a copy of the international application, unless it has been previously communicated by the International Bureau or unless it was originally filed in the USPTO; and (2) the basic national fee (see 37 C.F.R. § 1.492(a)). The 30-month time limit may not be extended. 37 C.F.R. § 1.495.

**WARNING:** Where the items are those which can be submitted to complete the entry of the international application into the national phase are subsequent to 30 months from the priority date the application is still considered to be in the international state and if mailing procedures are utilized to obtain a date the express mail procedure of 37 C.F.R. § 1.10 must be used (since international application papers are not covered by an ordinary certificate of mailing - See 37 C.F.R. § 1.8.

**NOTE:** Documents and fees must be clearly identified as a submission to enter the national state under 35 USC 371 otherwise the submission will be considered as being made under 35 USC 111. 37 C.F.R. § 1.494(f).

1. Applicant herewith submits to the United States Elected Office (EO/US) the following items under 35 U.S.C. 371:

- a. ☒ This express request to immediately begin national examination procedures (35 U.S.C. 371(f)).
- b. ☒ The U.S. National Fee (35 U.S.C. 371(c)(1)) and other fees (37 C.F.R. § 1.492) as indicated below:

## 2.Fees

CLAIMS FEE	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
[ ]*	TOTAL CLAIMS	9 =		x \$ 18.00 =	\$0
	INDEPENDENT CLAIMS	- 3 =		x \$ 78.00 =	0
	MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$260.00				0
BASIC FEE**	<p>[ ] U.S. PTO WAS INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where an International preliminary examination fee as set forth in § 1.482 has been paid on the international application to the U.S. PTO:</p> <p>[ ] and the international preliminary examination report states that the criteria of novelty, inventive step (non-obviousness) and industrial activity, as defined in PCT Article 33(2) to (4) have been satisfied for all the claims presented in the application entering the national stage (37 CFR 1.492(a)(4)) ..... \$96.00</p> <p>[ ] and the above requirements are not met (37 CFR 1.492(a)(1)) ..... \$670.00</p> <p>[X] U.S. PTO WAS NOT INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where no international preliminary examination fee as set forth in § 1.482 has been paid to the U.S. PTO, and payment of an international search fee as set forth in § 1.445(a)(2) to the U.S. PTO:</p> <p>[ ] has been paid (37 CFR 1.492(a)(2)) ..... \$760.00</p> <p>[ ] has not been paid (37 CFR 1.492(a)(3)) ..... \$970.00</p> <p>[X] where a search report on the international application has been prepared by the European Patent Office or the Japanese Patent Office (37 CFR 1.492(a)(5)) ..... \$840.00</p>				\$ 860.00
	Total of above Calculations				= \$ 860.00
SMALL ENTITY	Reduction by ½ for filing by small entity, if applicable. Affidavit must be filed. (note 37 CFR 1.9, 1.27, 1.28)				-
	Subtotal				\$ 860.00
	Total National Fee				\$ 860.00
	Fee for recording the enclosed assignment document \$40.00 (37 CFR 1.21(h)). (See Item 13 below). See attached "ASSIGNMENT COVER SHEET".				
TOTAL	Total Fees enclosed				\$ 860.00

\*See attached Preliminary Amendment Reducing the Number of Claims.

- i. ☒ A check in the amount of \$860.00 to cover the above fees is enclosed.
  - ii. ☐ Please charge Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_.
- A duplicate copy of this sheet is enclosed.

**\*\*WARNING:** "To avoid abandonment of the application the applicant shall furnish to the United States Patent and Trademark Office not later than the expiration of 30 months from the priority date: \* \* \* (2) the basic national fee (see § 1.492(a)). The 30-month time limit may not be extended." 37 C.F.R. § 1.495(b).

**WARNING:** If the translation of the international application and/or the oath or declaration have not been submitted by the applicant within thirty (30) months from the priority date, such requirements may be met within a time period set by the Office. 37 C.F.R. § 1.495(b)(2). The payment of the surcharge set forth in § 1.492(e) is required as a condition for accepting the oath or declaration later than thirty (30) months after the priority date. The payment of the processing fee set forth in § 1.492(f) is required for acceptance of an English translation later than thirty (30) months after the priority date. Failure to comply with these requirements will result in abandonment of the application. The provisions of § 1.136 apply to the period which is set. Notice of Jan. 3, 1993, 1147 O.G. 29 to 40.

3. ☒ A copy of the International application as filed (35 U.S.C. 371(c)(2)):

**NOTE:** Section 1.495 (b) was amended to require that the basic national fee and a copy of the international application must be filed with the Office by 30 months from the priority date to avoid abandonment "The International Bureau normally provides the copy of the international application to the Office in accordance with PCT Article 20. At the same time, the International Bureau notifies applicant of the communication to the Office. In accordance with PCT Rule 47.1, that notice shall be accepted by all designated offices as conclusive evidence that the communication has duly taken place. Thus, if the applicant desires to enter the national stage, the applicant normally need only check to be sure the notice from the International Bureau has been received and then pay the basic national fee by 30 months from the priority date." Notice of Jan. 7, 1993, 1147 O.G. 29 to 40, at 35-36. See item 14c below.

- a. ☐ is transmitted herewith.
- b. ☐ is not required, as the application was filed with the United States Receiving Office.
- c. ☒ has been transmitted
  - i. ☒ by the International Bureau.  
Date of mailing of the application (from form PCT/IB/308): \_\_\_\_\_.
  - ii. ☐ by applicant on \_\_\_\_\_.  
Date

4. ☒ A translation of the International application into the English language (35 U.S.C. 371(c)(2)):
- a. ☒ is transmitted herewith.
  - b. ☐ is not required as the application was filed in English.
  - c. ☐ was previously transmitted by applicant on \_\_\_\_\_.  
Date
  - d. ☐ will follow.

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5. [X] Amendments to the claims of the International application under PCT Article 19 (35 U.S.C. 371(c)(3)):

*NOTE: The Notice of January 7, 1993 points out that 37 C.F.R. § 1.495(a) was amended to clarify the existing and continuing practice that PCT Article 19 amendments must be submitted by 30 months from the priority date and this deadline may not be extended. The Notice further advises that: "The failure to do so will not result in loss of the subject matter of the PCT Article 19 amendments. Applicant may submit that subject matter in a preliminary amendment filed under section 1.121. In many cases, filing an amendment under section 1.121 is preferable since grammatical or idiomatic errors may be corrected." 1147 O.G. 29-40, at 36.*

- a. ☒ are transmitted herewith.
- b. ☐ have been transmitted
- i. ☐ by the International Bureau.  
Date of mailing of the amendment (from form PCT/IB/308): \_\_\_\_\_.
- ii. ☐ by applicant on \_\_\_\_\_.  
Date
- c. ☒ have not been transmitted as
- i. ☒ applicant chose not to make amendments under PCT Article 19.  
Date of mailing of Search Report (from form PCT/ISA/210): \_\_\_\_??.\_\_\_\_\_.
- ii. ☐ the time limit for the submission of amendments has not yet expired. The amendments or a statement that amendments have not been made will be transmitted before the expiration of the time limit under PCT Rule 46.1.
6. ☒ A translation of the amendments to the claims under PCT Article 19 (38 U.S.C. 371(c)(3)):
- a. ☐ is transmitted herewith.
- b. ☐ is not required as the amendments were made in the English language.
- c. ☒ has not been transmitted for reasons indicated at point 5(c) above.
7. ☐ A copy of the international examination report (PCT/IPEA/409)
- ☐ is transmitted herewith.
- ☐ is not required as the application was filed with the United States Receiving Office.
8. ☐ Annex(es) to the international preliminary examination report
- a. ☐ is/are transmitted herewith.
- b. ☐ is/are not required as the application was filed with the United States Receiving Office.
9. ☐ A translation of the annexes to the international preliminary examination report
- a. ☐ is transmitted herewith.
- b. ☐ is not required as the annexes are in the English language.
10. ☒ An oath or declaration of the inventor (35 U.S.C. 371(c)(4)) complying with 35 U.S.C. 115
- a. ☐ was previously submitted by applicant on \_\_\_\_\_.  
Date

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- b. ☐ is submitted herewith, and such oath or declaration
  - i. ☐ is attached to the application.
  - ii. ☐ identifies the application and any amendments under PCT Article 19 that were transmitted as stated in points 3(b) or 3(c) and 5(b); and states that they were reviewed by the inventor as required by 37 C.F.R. 1.70.
  - iii. ☒ will follow.

Other document(s) or information included:

- 11. ☒ An International Search Report (PCT/ISA/210) or Declaration under PCT Article 17(2)(a):
  - a. ☒ is transmitted herewith.
  - b. ☐ has been transmitted by the International Bureau.  
Date of mailing (from form PCT/IB/308): \_\_\_\_\_.
  - c. ☐ is not required, as the application was searched by the United States International Searching Authority.
  - d. ☐ will be transmitted promptly upon request.
  - e. ☐ has been submitted by applicant on \_\_\_\_\_.  
Date

- 12. ☒ An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98:
  - a. ☒ is transmitted herewith.  
Also transmitted herewith is/are:
    - ☐ Form PTO-1449 (PTO/SB/08A and 08B).
    - ☐ Copies of citations listed.
  - b. ☐ will be transmitted within THREE MONTHS of the date of submission of requirements under 35 U.S.C. 371(c).
  - c. ☐ was previously submitted by applicant on \_\_\_\_\_.  
Date

- 13. ☐ An assignment document is transmitted herewith for recording.

A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

- 14. ☒ Additional documents:
  - a. ☒ Copy of request (PCT/RO/101)
  - b. ☐ International Publication No. \_\_\_\_\_
    - i. ☐ Specification, claims and drawing
    - ii. ☐ Front page only
  - c. ☐ Preliminary amendment (37 C.F.R. § 1.121)
  - d. ☐ Other

15. ☒ The above checked items are being transmitted  
 a. ☒ before 30 months from any claimed priority date.  
 b. ☐ after 30 months.
16. ☐ Certain requirements under 35 U.S.C. 371 were previously submitted by the applicant on \_\_\_\_\_, namely:
- \_\_\_\_\_
- \_\_\_\_\_
- \_\_\_\_\_

### AUTHORIZATION TO CHARGE ADDITIONAL FEES

**WARNING:** *Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges if extra claims are authorized.*

**NOTE:** *"A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 C.F.R. § 1.136(a)(3).*

**NOTE:** *"Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).*

☒ The Commissioner is hereby authorized to charge the following additional fees that may be required by this paper and during the entire pendency of this application to Account No. 04-1105.

☒ 37 C.F.R. 1.492(a)(1), (2), (3), and (4) (filing fees)

**WARNING:** *Because failure to pay the national fee within 30 months without extension (37 C.F.R. § 1.495(b)(2)) results in abandonment of the application, it would be best to always check the above box.*

☒ 37 C.F.R. 1.492(b), (c) and (d) (presentation of extra claims)

**NOTE:** *Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 C.F.R. § 1.492(d)), it might be best not to authorize the PTO to charge additional claim fees, except possible when dealing with amendments after final action.*

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- ☒ 37 C.F.R. 1.17 (application processing fees)  
☒ 37 C.F.R. 1.17(a)(1)-(5)(extension fees pursuant to § 1.136(a).  
☐ 37 C.F.R. 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. 1.311(b))

*NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 C.F.R. § 1.311(b).*

*NOTE: 37 C.F.R. 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying . . . issue fee." From the wording of 37 C.F.R. § 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.*

- ☐ 37 C.F.R. § 1.492(e) and (f) (surcharge fees for filing the declaration and/or filing an English translation of an International Application later than 30 months after the priority date).

  
SIGNATURE OF PRACTITIONER

Peter F. Corless

(type or print name of practitioner)

Dike, Bronstein, Roberts & Cushman  
Intellectual Property Practice Group  
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Boston, MA 02109

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Docket 55542  
IN THE UNITED STATES PATENT OFFICE

In re applications. Heckmann

Group: N/A

Serial # 09/743,244

Examiner: N/A

Filed: 1/5/01

For: Porous Ceramics

Assistant Commissioner of Patents  
Washington, D.C. 20231

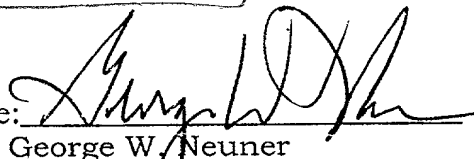
Sir:

CHANGE OF MAILING ADDRESS

Applicant requests that all further communications from the Patent and Trademark Office in connection with the subject application be sent to the following address:

**Dike, Bronstein, Roberts & Cushman**  
**Intellectual Property Practice Group**  
**EDWARDS & ANGELL**  
P.O. Box 9169  
Boston, MA 02209  
Tel.: (617) 523-3400  
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Date: April 6 2001

Name:   
George W. Neuner  
Registration No. 26,964

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DESCRIPTION

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Porous ceramics

This invention relates to a porous ceramic and to a process for producing it.

Highly porous ceramics are increasingly being used as filter systems, as implants in medical technology and as supports for catalysts. There are numerous processes for producing them, only two of which will be cited here:

The production from aerogels and the burning-out of previously admixed organic additives.

The areas of use of ceramics such as these depend on their chemical and thermal stability, on their permeability, on their specific surface and on the length of the diffusion paths to their active surface.

The materials are selected based on requirements imposed by their area of use and stability; their pore size, pore size distribution and pore shape are selected based on the requirements of permeability, diffusion path and surface area. The importance of these properties to the use of these ceramic substances is clear: good stability enables them to be used even with aggressive media and at high temperatures, whilst good permeability results in a low pressure drop during operation and thus facilitates low energy consumption; a high specific surface results in a high density of adsorption centres and/or reaction centres; short

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diffusion paths enable active centres to be reached by flows of material in reasonable timescales.

Unfortunately, only partial success has been achieved hitherto in optimising these four important properties simultaneously in order to obtain high stability, a low resistance to flow, a high specific surface and short diffusion paths. Good permeability cannot be achieved with randomly oriented powdered materials or random arrangements of materials which are subsequently sintered, because these are macroscopically isotropic and also exhibit a high resistance to flow (one known example of a sintered, randomly oriented powdered material is a glass frit which is fused into chemical apparatuses). Instead, macroscopically anisotropic arrangements of particles are required, and what is required in practice is therefore systems of tubes or capillaries which are open at both ends and which have aperture diameters of the same magnitude. However, it has hitherto only been possible to produce systems such as these with tube and/or capillary spacings which are large in absolute terms. The regions between the capillaries/tubes can only be reached via long diffusion paths. For this reason, a high specific internal surface of the wall material is incapable of having the desired effect, since it is only the edge regions thereof around the tubes/capillaries which can be reached by flows of substance within a reasonably short timescale.

Currently, ceramics through which capillaries or tubes pass can only be produced by extrusion methods. The smallest diameter which can thereby be achieved is 200  $\mu\text{m}$ . The spacings between the capillaries/tubes are about 600  $\mu\text{m}$ .

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commercially available. Even the patent and scientific literature contains no references to structures such as these.

It is only the document EP-A-0479553 that describes porous ceramics with a high porosity and a narrow pore size distribution which are obtained by preparing a dilute slurry of a ceramic starting material in a solution of a high molecular weight organic compound such as ammonium alginate, which can be converted into a gel by reaction with an acid or with tri- or polyvalent cations or by heating or cooling. The slurry is brought into contact with a liquid or with a gel in which the acid or the tri- or polyvalent cations are present, or is heated or cooled, in order to obtain a ceramic gel substance which is subsequently calcined. These porous ceramics exhibit improved resistance and mechanical strength and are thus suitable as high-temperature catalyst supports.

The underlying object of the present invention is therefore to provide a ceramic body with a high stability, a low resistance to flow, a high specific surface and short diffusion paths, as well as a process for the production thereof.

The present invention relates to a porous ceramic, which is produced by:

- a) mixing an aqueous solution of a suitable ionotropically orientable polyanion, either with

- oxides, hydroxides or hydrated oxides, which are present in the form of a sol, of the metals Al, Zr, Ti and Nb,
  - or with finely crystalline oxides, hydroxides or hydrated oxides, which are present in suspension, of these metals,
  - or with finely crystalline tricalcium phosphate or apatite which are present in suspension,
- b) bringing the mixed sol obtained as in a) or the suspension obtained as in a) into contact with a solution of a salt of a di- or trivalent metal cation in order to produce an ionotropic gel body,

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solution of a salt of a di- or trivalent metal cation in order to produce an ionotropic gel body,

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- c) compacting the gel body by introducing it into electrolyte solutions which further enhance the syneresis of the polyelectrolyte which was originally formed,
- d) washing the gel body with water and subsequently impregnating it with a readily volatile, water-miscible solvent,
- e) freeing the anhydrous gel body obtained as in d) from the readily volatile water-miscible solvent,
- f) burning out the organic constituents from the dry gel body obtained as in e),
- g) sintering the product obtained as in f).

Ionotropic gels are formed when a dilute aqueous solution of a suitable anionic polymer, for example a solution of a sodium alginate or of a sodium pectinate, or of sodium cellulose xanthogenate, sodium xanthate or sodium hyaluronate, is brought into contact with a solution of a divalent cation such as  $\text{Cu}^{2+}$  or  $\text{Ca}^{2+}$  or with a solution of a trivalent cation such as  $\text{Al}^{3+}$  or  $\text{La}^{3+}$ . This is effected, for example, by adding the solution of the polyanion drop-wise to the solution of the metal cation or by adding the solution of the metal cation drop-wise to the solution of the polyanion, or by coating one solution with the other in the absence of convection. The proportion by weight of the polyanion in the sol can range between 0.25 and 5.0 percent by weight. Proportions by weight from 0.5 to 2.0 percent by weight are particularly suitable. The concentrations of the

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metal salt solutions are greater than  $10^{-3}$  M and are less than the respective saturation concentration of the salt in water. Concentrations between  $10^{-1}$  and 2 M are most suitable. After the formation of a membrane-like precipitate at the phase boundary between the two liquids, which is termed the primary membrane, oriented diffusion occurs of the low molecular weight electrolyte into the solution of the polymer. However, the precipitation which continues to occur at this location does not result in amorphous precipitate, but in a gel which is structured in three dimensions.

Regularly arranged capillaries are then formed, which are of practically identical size and which are circular in cross-section, the walls of which capillaries consist of the precipitated product and the lumina of which absorb the water evolved during precipitation. The stability of the gel is therefore based on the fact that the di- or trivalent cations crosslink the molecules of the polymer with each other and thus impart a certain mechanical strength to the capillary walls. The capillaries are all parallel to each other in the direction of diffusion of the electrolyte and can reach a length of a few centimetres. The arrangement of the capillaries is almost perfectly hexagonal and their radii slowly increase in the direction of diffusion of the metal cation, with a gradient of about 5 %. The diameter of the capillaries of the gel can be adjusted within wide limits via the viscosity of the polyanion and the type of polyvalent cation. The lower limit which could be achieved hitherto was about 5  $\mu\text{m}$ , and the upper limit was about 300  $\mu\text{m}$ . If the gels are produced by coating the two solutions, their strength in most cases is sufficient to enable them to be cut - starting at the top - into slices, the smallest thickness of which is about 1/2 mm and maximum thickness of which can be about 2 cm. Due to the conicity of the

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capillaries, which are perpendicular to the slices, capillaries with arbitrarily predeterminable diameters can be obtained in the gel, depending on the depth of cut.

The alginate which is cited as an example here has been investigated particularly thoroughly with regard to its capacity for ionotropic orientation. Moreover, the capillary gels of this alginate are particularly regular. Under comparable experimental conditions, however, other substances, which were not investigated in such detail, also form patterns of capillaries which only exhibit qualitative differences from those of the alginate.

Amongst others, these latter substances include organic polyions such as pectinates, cellulose xanthogenates, xanthates, hyaluronates, chondroitin sulphates, salts of carboxymethyl cellulose, of carboxyl cellulose and of chitosan; they also include complexes of polyanions (symplexes) and polycations, and finally they also include inorganic substances such as vanadium pentoxide and mixed organic/inorganic substances such as mercury sulphosalicylate. These substance are therefore all polyelectrolytes.

According to the invention, it is possible to use ionotropic capillary gels as template structures for the production of crack-free, porous ceramics, the geometric structure of which is completely identical to the corresponding structure of the gels. It is only the dimensions of the porous ceramic structures as a whole which are somewhat smaller than those of the gel, as a result of drying and sintering. At first glance, the external appearance of ceramics such as these is the same as that of porous sintered bodies made of glass. As distinct from the latter, however, the ceramic is not isotropic, but is highly anisotropic as a result of the

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capillaries. On a second glance, this can be recognised by the iridescent sheen of the ceramic surface, which is reminiscent of the appearance of facets.

The diameters of the capillaries of the ceramic have values between 1 and 200  $\mu\text{m}$ , and the spacings between the capillaries are about the same size as the capillary diameter. The free surface of the ceramic, which is formed by the capillary apertures, amounts to about 50 % of its total surface area, and there are about 50,000 capillaries per  $\text{cm}^2$  of surface. The porosity or proportion of voids of the ceramic ranges between 75 % and 85 % of the total volume thereof.

The porosity of the ceramic can be analysed in greater detail by means of mercury porosimetry. It is found that a ceramic produced from alginate/boehmite mixed sols, for example, has a trimodal pore size distribution, whereas a ceramic obtained from suspended alumina has a bimodal distribution. In both these cases, the capillaries constitute the population of the largest pores and the interstices between the alumina particles of the pore walls constitute the population of the second largest pores. Moreover, when boehmite is used the spaces between the individual crystallites of boehmite constitute a third population, which is manifested as an additional internal porosity of the alumina particles in the capillary walls. The first population (capillaries) has a pore size maximum at about 10  $\mu\text{m}$ , the second at about 130 nm, and the third at 58 nm.

Production of the ceramic necessitates that either a sol of a metal hydroxide or of a hydrated metal oxide is produced in the alginate sol or that a slurry of a finely crystalline

metal oxide, metal hydroxide or hydrated metal oxide is admixed with the alginate sol.

The term "finely crystalline" denotes average particle sizes from 10 nm to 1 mm, preferably from 100 nm to 500 nm.

The formation of the ionotropic capillary gels from mixed sols proceeds exactly as does the formation thereof from unmodified sols, except that the inorganic component accumulates in the capillary walls. In the latter gel bodies, the density of the solid particles in the capillary walls is still so low that a ceramic produced therefrom does not yet possess the desired mechanical strength even after being subjected to all the other process steps. It is therefore necessary to subject the gel body to a shrinkage process, in order further to increase the particle density. For this purpose, the syneresis which occurred with the original formation of the gel has to be further enhanced, and additional proportions of the water which is bound in the gel have to be discharged in the capillary lumina. In order to achieve this, there are various practical options which are all theoretically based on the same principle. The osmotic pressure in the regions of the capillary walls has to be reduced, and the osmotic pressure in the lumina has to be increased. Increasing the pressure in the lumina does not necessitate further discussion; reducing the pressure in the regions of the capillary walls is effected by ion exchange. The polyvalent metal cations which were originally required for gel formation are replaced by more strongly bound ions, which in the best case are even more weakly hydrated. Amongst other type of ions, the latter can be protons, with the gel body being incubated in baths of hydrochloric acid of increasing concentrations, for example, in order to effect further

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compaction. In order to effect the exchange of metal ions, it is particularly effective if a solution of a poly- or oligo-electrolyte, the solid-state ions of which bear the opposite charge to the solid-state ions of the polyion which was originally formed, is introduced into the capillary lumina. In particular, oppositely charged, high molecular weight electrolytes are mutually precipitated to form precipitates of high density, which are insoluble in most solvents. These are termed "symplexes". If the polyion which was originally gel-forming is a polyanion, an alginate, for example, the ions which are suitable for symplex formation include all polycations, e.g. polyvinylamine, polyallylamine, polyvinylpyridine or polyethylene-imine cations, and also include polycations of biological origin such as chitosan; examples of suitable oligocations include pentaethylenhexamine or, again, biological substances such as protamines and histones. Charged oligomers and polymers which are suitable for symplex formation also include micelles of ionic surface-active agents.

For symplex formation also, it is advantageous to increase the concentrations of the precipitating polyions by adding the latter in portions.

During ion exchange, the gel bodies shrink in every dimension to about half their original linear dimensions, and ion exchange has to be carried out particularly carefully since the gel substances exhibit a pronounced tendency towards crack formation during shrinkage.

After ion exchange, the gel substances are subjected to a series of washing and dewatering steps in which water is displaced by a readily volatile organic, water-miscible solvent, e.g. acetone. This solvent is also removed after

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dewatering. Examples of processes which are suitable for this purpose include supercritical drying in carbon dioxide, pressing out the liquid with the aid of fine-pored earthenware slabs, or simply allowing the batch to stand in air under ambient conditions. After the solvent has been removed, a typical "green body" is formed. This is heated according to an appropriate temperature-time programme, whereupon the organic template structure is carbonized or burned. Finally, the finished ceramic is formed by sintering. The organic template substances are routinely burned out at 600°C for two hours. The completion of burn-out in each case is indicated by the colour of the sample changing from black to white. Temperatures of 800°C to 1400°C are required for sintering the samples. The duration of firing ranges from two to ten hours. The temperature and duration of the firing operation are ultimately determined based on the magnitude of the specific surface of the ceramic and the mechanical performance thereof, and are re-determined from case to case depending on the requirements imposed on the final product.

The ceramic according to the invention can be produced in various geometric shapes, depending on the sphere of use thereof. The ceramics can be employed for particularly diverse uses if they are in the form of frits of defined geometry which can readily be incorporated in predetermined apparatuses or parts of apparatuses. Frits such as these are plate-shaped and can be produced in both round and polygonal form. Their thicknesses range from 2 to 4 mm. The edge lengths of polygonal plates are about 100 mm long, as are the diameters of round discs.

Another form of the ceramic consists of a granular material comprising predominantly spherical grains a few

It is sometimes sufficient simply to comminute the ceramic mechanically and then to obtain various sieve fractions therefrom. It is important here that the particle dimensions remain significantly larger than the pore diameter, because each particle should contain a plurality of capillaries.

In the form of a frit, the ceramic can also be employed as a permeable sorbent for chromatographic purposes. A ceramic made of alumina is suitable for this purpose.

If the ceramic is comminuted in a suitable mill so that the resulting particles are no smaller than about 100  $\mu\text{m}$  and thus still contain a number of intact capillaries, an inorganic material is available which can be processed together with organic polymers, for example acrylic resins, to form composite materials with interesting new properties, for use as dental fillings for example. If the porous capillary ceramic (optionally after covering the surface thereof with a coupling agent) is impregnated with monomers or oligomers of a polymerisable substance, the shrinkage

which unavoidably occurs in the interior of the capillaries during polymerisation is particularly low. Consequently, dental fillings made of a composite material which contains a high proportion of capillary ceramic only exhibit a slight tendency to form cracks due to shrinkage between the dentine and the filling on curing.

The invention is explained in more detail by the examples given below.

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## Example 1

A ceramic capillary frit produced from a mixed sol consisting of boehmite and sodium alginate.

In a first step, a boehmite sol is produced. The proportion by weight of boehmite in this sol is initially about 3 %. In a second step, the boehmite sol is concentrated to a boehmite content of 16.5%. In a third step, one proportion by weight of the concentrated boehmite sol is mixed with four proportions by weight of a  $6 \times 10^{-2}$  M solution of sodium sulphate. After homogenisation, one proportion by weight of this sulphate-containing suspension is introduced into one proportion by weight of a sodium alginate sol, which contains 2 % by weight of sodium alginate, and is again homogenised therein. At this point, a fairly stable boehmite / alginate mixed sol is present.

The subsequent steps comprise: coating the mixed sol with 1 M  $\text{Cu}(\text{NO}_3)_2$  in the absence of convection, allowing the gel to mature for 10 hours (i.e. forming the capillary structure), cutting gel slices, effecting ion exchange ( $\text{Cu}^{2+}$  replaced by  $2\text{H}^+$ ) by successively introducing the gel body into baths of increasing hydrochloric acid concentration, washing out the remaining acid with water and replacing the water by acetone, removing the acetone by suction through porous earthenware slabs, burning out the organic constituents of the green body at  $600^\circ\text{C}$  for 2 hours, and sintering at  $1400^\circ\text{C}$  for 2 hours to form the capillary frit. The ceramic body is cut to its final dimensions and is optionally lapped.



## Example 2

A ceramic capillary frit produced from a suspension of alumina in a sodium alginate sol.

A fine crystalline alumina powder with an average particle size of 350 nm is suspended in water. The proportion by weight of alumina in this suspension is 8%.

One proportion by weight of this suspension is then mixed with one proportion by weight of a sodium alginate sol (2 % by weight). After homogenisation, further processing was effected corresponding to Example 1, starting with coating by a copper nitrate solution.

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CLAIMS

1. A porous ceramic, obtainable by:

a) mixing an aqueous solution of a suitable ionotropically orientable polyanion, either with

- oxides, hydroxides or hydrated oxides, which are present in the form of a sol, of the metals Al, Zr, Ti and Nb,
- or with finely crystalline oxides, hydroxides or hydrated oxides, which are present in suspension, of these metals,
- or with finely crystalline tricalcium phosphate or apatite which are present in suspension,

b) bringing the mixed sol obtained as in a) or the suspension obtained as in a) into contact with a solution of a salt of a di- or trivalent metal cation in order to produce an ionotropic gel body,

c) compacting the gel body by introducing it into electrolyte solutions which further enhance the syneresis of the polyelectrolyte which was originally formed,

d) washing the gel body with water and subsequently impregnating it with a readily volatile, water-miscible solvent,

- e) freeing the anhydrous gel body or gel bodies obtained as in d) from the readily volatile, water-miscible solvent,
- f) burning out the organic constituents from the dry gel body or the dry gel bodies obtained as in e),
- g) sintering the product obtained as in f).

2. A porous ceramic according to claim 1, characterised in that it is formed as a capillary frit and is obtainable by:

- a) mixing an aqueous solution of a suitable ionotropically orientable polyanion, either with
  - oxides, hydroxides or hydrated oxides, which are present in the form of a sol, of the metals Al, Zr, Ti and Nb,
  - or with finely crystalline oxides, hydroxides or hydrated oxides, which are present in suspension, of these metals,
  - or with finely crystalline tricalcium phosphate or apatite which are present in suspension,
- b) coating the mixed sol obtained as in a) or the suspension obtained as in a) with a solution of a salt of a di- or trivalent metal cation in

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order to produce an ionotropic gel substance and cutting said gel body into slices,

- c) compacting the gel body by introducing it into electrolyte solutions which further enhance the syneresis of the polyelectrolyte which was originally formed,
- d) washing the gel body with water and subsequently impregnating it with a readily volatile, water-miscible solvent,
- e) freeing the anhydrous gel slices obtained as in d) from the readily volatile, water-miscible solvent,
- f) burning out the organic constituents from the dry gel slices obtained as in e),
- g) sintering the product obtained as in f).

3. A process for producing a porous ceramic, characterised by the following steps:

- a) mixing an aqueous solution of a suitable ionotropically orientable polyanion, either with
  - oxides, hydroxides or hydrated oxides, which are present in the form of a sol, of the metals Al, Zr, Ti and Nb,

- or with finely crystalline oxides, hydroxides or hydrated oxides, which are present in suspension, of these metals,
  - or with finely crystalline tricalcium phosphate or apatite which are present in suspension,
- b) bringing the mixed sol obtained as in a) or the suspension obtained as in a) into contact with a solution of a salt of a di- or trivalent metal cation in order to produce an ionotropic gel body,
- c) compacting the gel body by introducing it into electrolyte solutions which further enhance the syneresis of the polyelectrolyte which was originally formed,
- d) washing the gel body with water and subsequently impregnating it with a readily volatile, water-miscible solvent,
- e) freeing the anhydrous gel body or gel bodies obtained as in d) from the readily volatile, water-miscible solvent,
- f) burning out the organic constituents from the dry gel body or the dry gel bodies obtained as in e),
- g) sintering the product obtained as in f).

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4. A process according to claim 3 for producing a ceramic capillary frit, characterised by the following steps:

a) mixing an aqueous solution of a suitable ionotropically orientable polyanion, either with

- oxides, hydroxides or hydrated oxides, which are present in the form of a sol, of the metals Al, Zr, Ti and Nb,
- or with finely crystalline oxides, hydroxides or hydrated oxides, which are present in suspension, of these metals,
- or with finely crystalline tricalcium phosphate or apatite which are present in suspension,

b) coating the mixed sol obtained as in a) or the suspension obtained as in a) with a solution of a salt of a di- or trivalent metal cation in order to produce an ionotropic gel body, and cutting said gel body into slices,

c) compacting the gel body by introducing it into electrolyte solutions which further enhance the syneresis of the polyelectrolyte which was originally formed,

d) washing the gel body with water and subsequently impregnating it with a readily volatile, water-miscible solvent, ,

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- e) freeing the anhydrous gel slices obtained as in d) from the readily volatile water-miscible solvent,
- f) burning out the organic constituents from the dry gel slices obtained as in e),
- g) sintering the product obtained as in f).

- 5. Use of the ceramic according to claim 1 as a catalyst or as a catalyst support.
- 6. Use of a granular ceramic material produced from the ceramic according to claim 1 as a ceramic component for composite materials.
- 7. A use according to claim 6, characterised in that in addition to the ceramic the composite material comprises a synthetic resin and optionally a coupling agent.
- 8. Use of the composite material as defined in claim 7 as a dental material, particularly as a dental cement.
- 9. Use of the ceramic capillary frit according to claim 2 as a catalyst, a catalyst support, a reversible flow filter and as a slab-like sorbent for chromatography columns.

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ABSTRACT

Porous ceramics are described, which are produced by

- a) mixing an aqueous solution of a suitable ionotropically orientable polyanion, either with
- oxides, hydroxides or hydrated oxides, which are present in the form of a sol, of the metals Al, Zr, Ti and Nb,
  - or with finely crystalline oxides, hydroxides or hydrated oxides, which are present in suspension, of these metals,
  - or with finely crystalline tricalcium phosphate or apatite which are present in suspension,
- b) bringing the mixed sol obtained as in a) or the suspension obtained as in a) into contact with a solution of a salt of a di- or trivalent metal cation in order to produce an ionotropic gel body,
- c) compacting the gel body by introducing it into electrolyte solutions which further enhance the syneresis of the polyelectrolyte which was originally formed,
- d) washing the gel body with water and subsequently impregnating it with a readily volatile, water-miscible solvent,



- e) freeing the anhydrous gel body or gel bodies obtained as in d) from the readily volatile, water-miscible solvent,
- f) burning out the organic constituents from the dry gel body or the dry gel bodies obtained as in e),
- g) sintering the product obtained as in f).

A capillary frit is also described. Moreover, the invention describes the use of these materials as a catalyst or as a catalyst support, as a ceramic component for composite materials, as a reversible flow filter and as a slab-like sorbent for chromatography columns, as well as the use of a composite material, which is produced from a granular material of the ceramics which are described, as a dental material, particularly as a dental cement.

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Docket No. 55542  
Page 1 of 3**Declaration and Power of Attorney for Patent Application**  
**English Language Declaration**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**POROUS CERAMICS**

the specification of which

(check one)

☐ is attached hereto.  
☒ was filed on January 5, 2001 as United States Application No. or PCT  
Application No. 09/743,244  
and was amended on \_\_\_\_\_  
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

<u>DE 198 30 795.0</u> (Number)	<u>Germany</u> (Country)	<u>09 July 1998</u> (Day/Month/Year Filed)	<input type="checkbox"/>
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	<input type="checkbox"/>
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	<input type="checkbox"/>

Page 2 of 3

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

_____	_____
(Application Serial No.)	(Filing Date)
_____	_____
(Application Serial No.)	(Filing Date)
_____	_____
(Application Serial No.)	(Filing Date)

I hereby claim the benefit under 35 U.S.C. Section 120 of the United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark office all information known to me to be material to patentability as defined in Title 37, C.F.C., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

PCT/EP99/04841	09 July 1999	Pending
_____	_____	_____
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)
_____	_____	_____
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)
_____	_____	_____
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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